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# Study of Combustion Characteristics of Hydrocarbon Nanofuel Droplets



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# Objectives and Overview

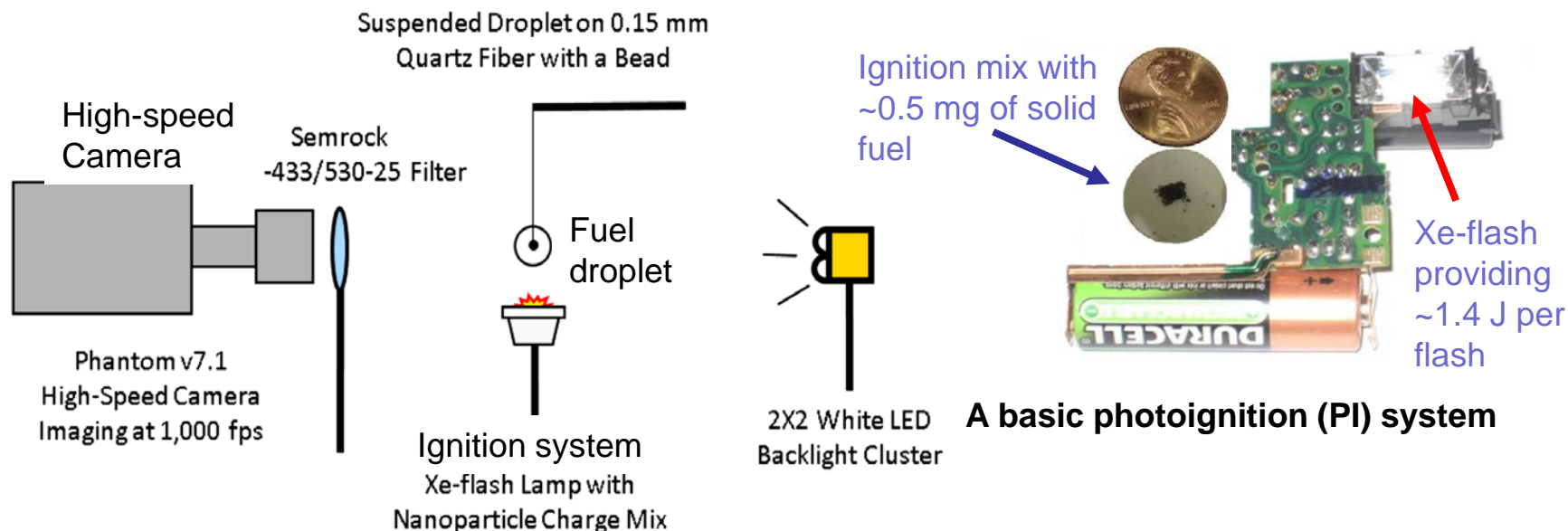


## Goal of the Project:

- Control of combustion dynamics of hydrocarbon fuels through solid nano-energetic additives.
- This is a multi-task project, which includes the following steps:
  - **Combustion Characteristics of Suspended Droplets of Hydrocarbon Fuels:**
    - Create baseline results for hydrocarbon fuels at ambient conditions (completed.)
    - Identify nano-energetic fuel additives, which could potentially significantly influence combustion characteristics (current work.)
  - **Study of Nanofuel Spray Burning at High Pressures:**
    - Study combustion characteristics and ignition transient for nanofuel sprays under subcritical ( $<450$  psi) conditions in a sacrificial pressure vessel.
    - Investigate combustion dynamics of nanofuel sprays under acoustic forcing at supercritical conditions ( $>600$  psi) in our combustion inability facility.



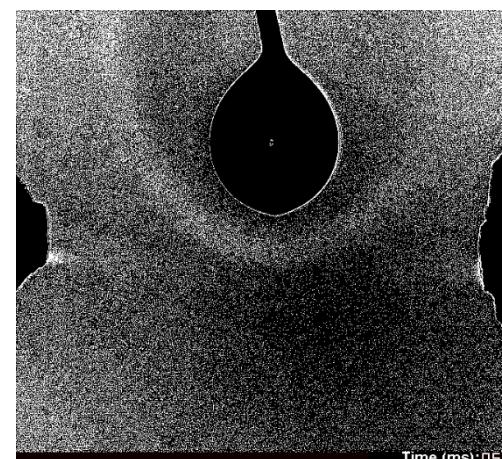
# Ignition of a Suspended Droplet by Photoignition and Plasma Arc Ignitor



Activation of the Xe-flash leads to photoignition of Al nanoparticles



**PI plume in action**



**Plasma Arc Ignitor in action**



# Justification for Using Fast-acting Ignition Methods



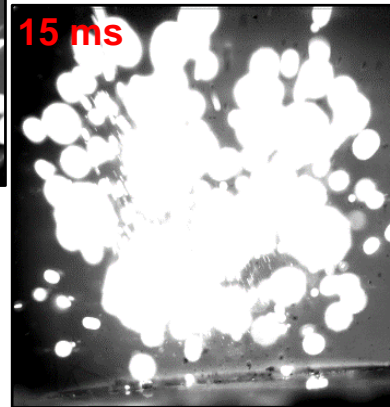
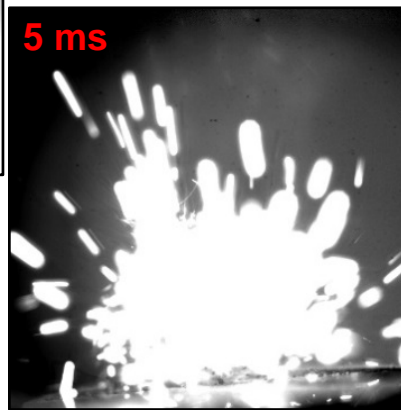
- Photoignition (PI) and plasma arc ignitor (PAI) proved to be well-suited for the study of burning characteristics of fuel droplets.
- Advantages of PI and PAI compared to conventional ignition methods:
  - Short ignition duration  $<120$  ms vs  $>500$  ms,
  - High ignition temperature ( $>2000$  K) vs  $<1300$  K, and
  - Much lower heat transfer due to low energy consumption
- The short ignition duration facilitates the observation of ignition delay, the onset of quasi steady burning and the “two-stage ignition” in droplets.
- PI is applicable up to 1000 psi and PAI is applicable  $<250$  psi.
- PI ejects burning nanoparticles (typically nAl) that may:
  - Potentially contaminate the fuel droplet
  - May initially interfere with imaging due bright particles
- We first used PI for neat fuels, but later we switched to plasma arc ignitor due to potential contamination of the droplet
- PAI is least intrusive with no interference with flame imaging.



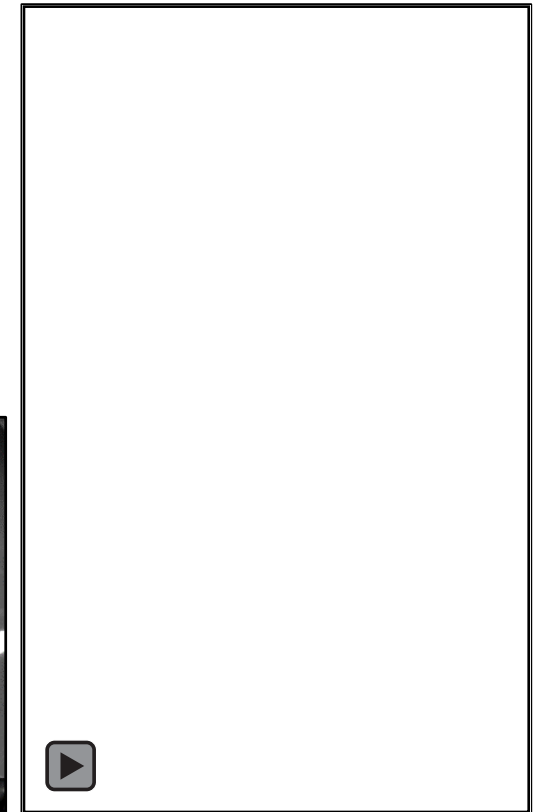
# Photoignition of Al NPs as it Leads to the Combustion of a Fuel Droplet



Burning of Al NPs after Xe-Flash activation



Al NPs burn very hot ( $>2000$  K), the burning may last  $\sim 100$  ms



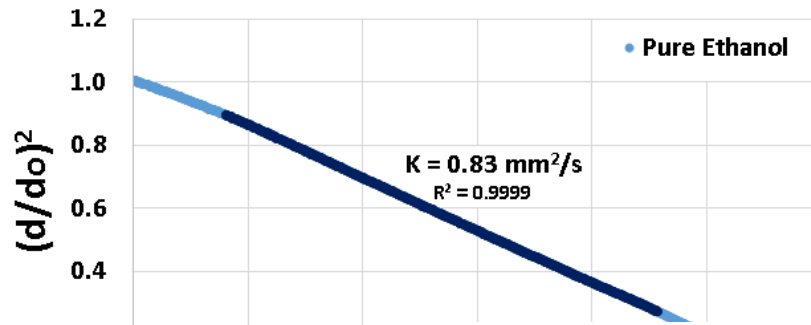
We used two fast-acting ignition methods, ( $\sim 100$  ms), either photoignition or plasma arc ignition. We also performed a few Ni-Cr heating coil ignition ( $\sim 500$  ms), to confirm that the ignition method had no adverse effects on the burn duration

Burning of a suspended  
RP-2 droplet with  
 $D = 1.4 \pm 0.1$  mm

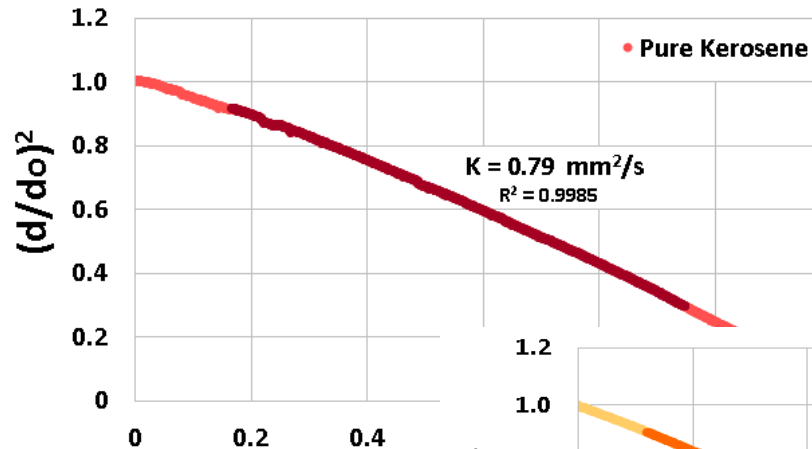




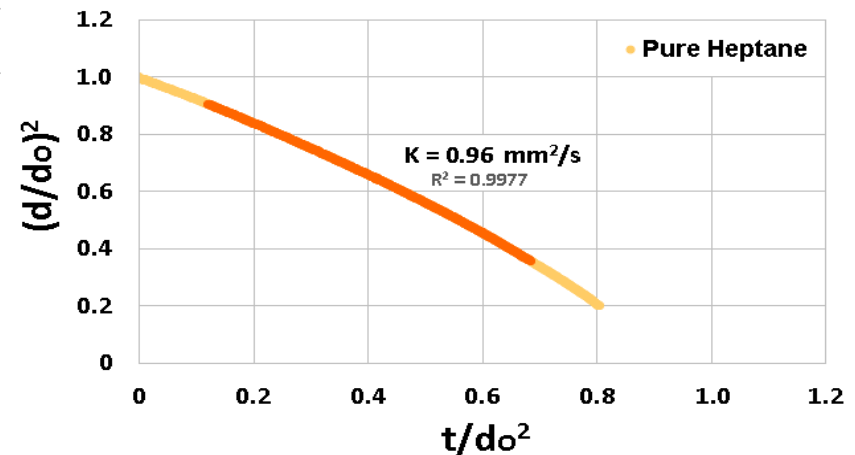
# Evaluation of Burning Rate Constant, $K$ (from Diameter Tracking Data for Different Fuels)



$K_{mid.,70}$  (70% of data around mid point), transient effects at the beginning and the end are excluded  
Quasi steady burning of ethanol is most linear, so  $K$  is least sensitive to the evaluation method



RP-2 burning curve is in between the other two



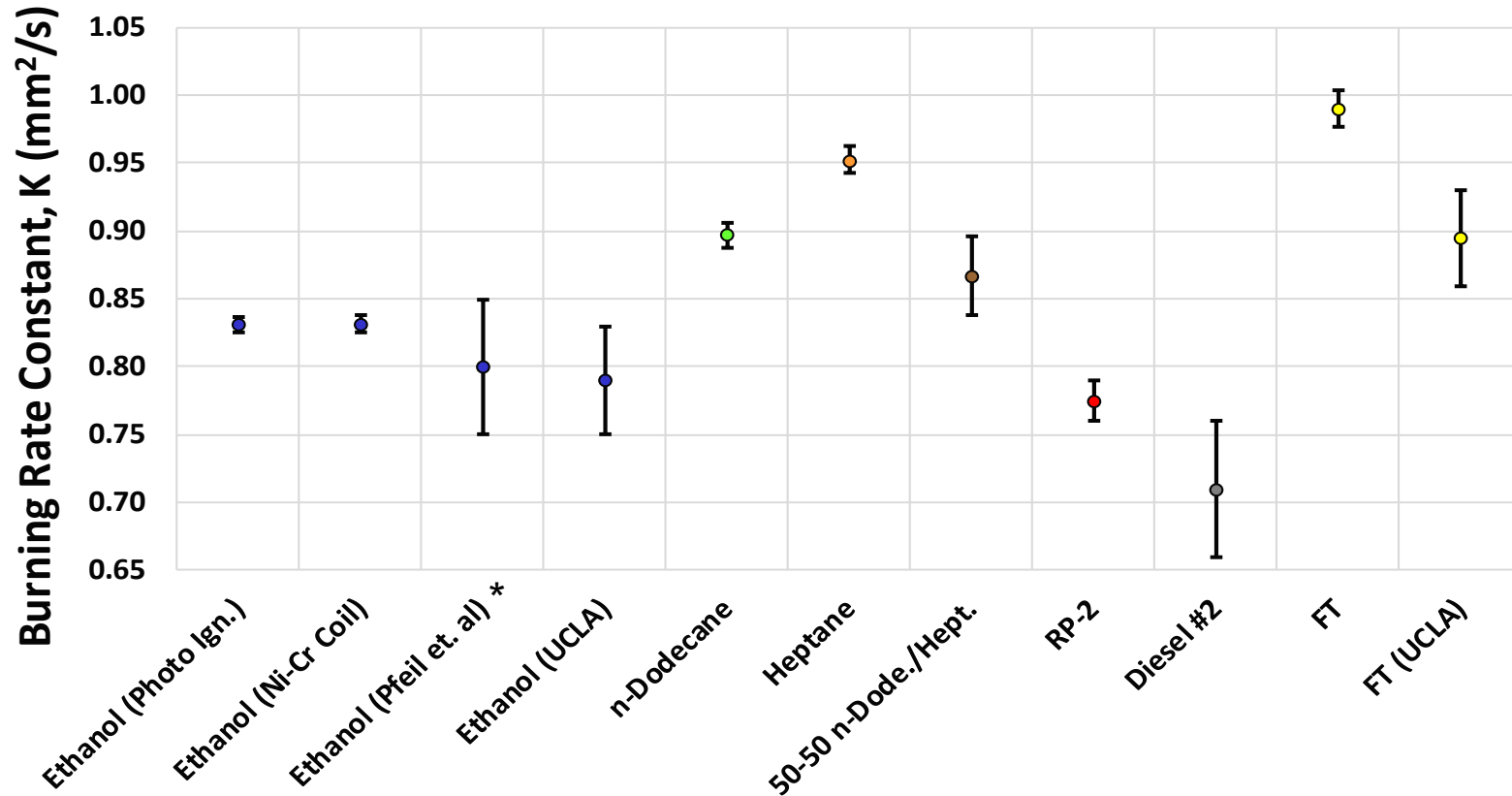
Quasi steady burning of Heptane is most nonlinear, so  $K$  is quite sensitive to the evaluation method and any deviations from  $K_{mid.,70}$  results in the most changes in  $K$  that in some fuels can be up to 25%.



# Burning Rate Constants ( $K$ ) for Different Neat Fuel Droplets



$K$  values are consistent with other labs



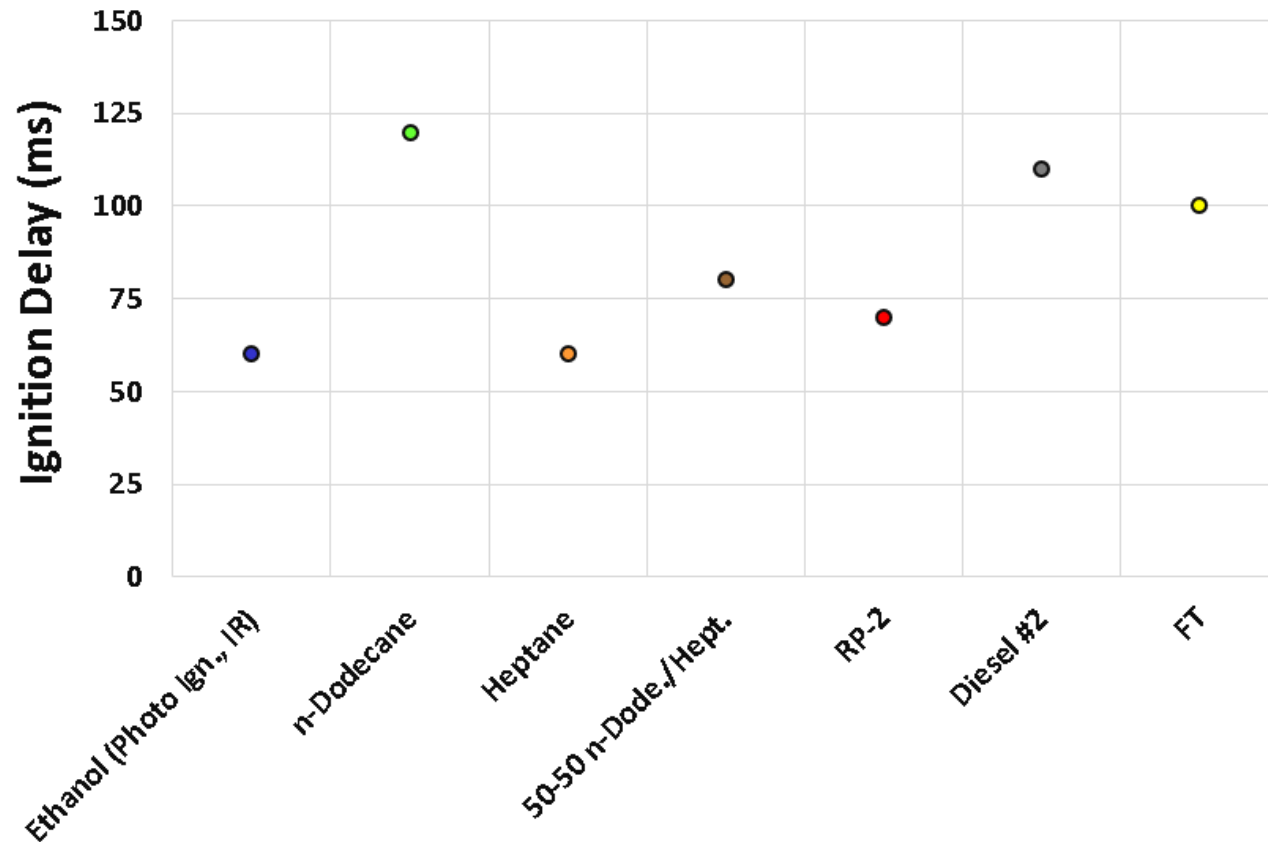
\* Pfeil et., al, *Combustion and Flame* (2013)

- $K$  values are based on multiple series of 15 tests for each fuel (-Diesel #2.),  $D = 1.4 \pm 0.1$  mm.
- For consistency, we only report  $K = K_{mid.,70}$ , though it may not be the best value in specific cases
- Statistical uncertainties associated with the evaluation method for  $K$  can be as large as  $\pm 10\%$





# Ignition Delay for Neat Hydrocarbon Fuel Droplets

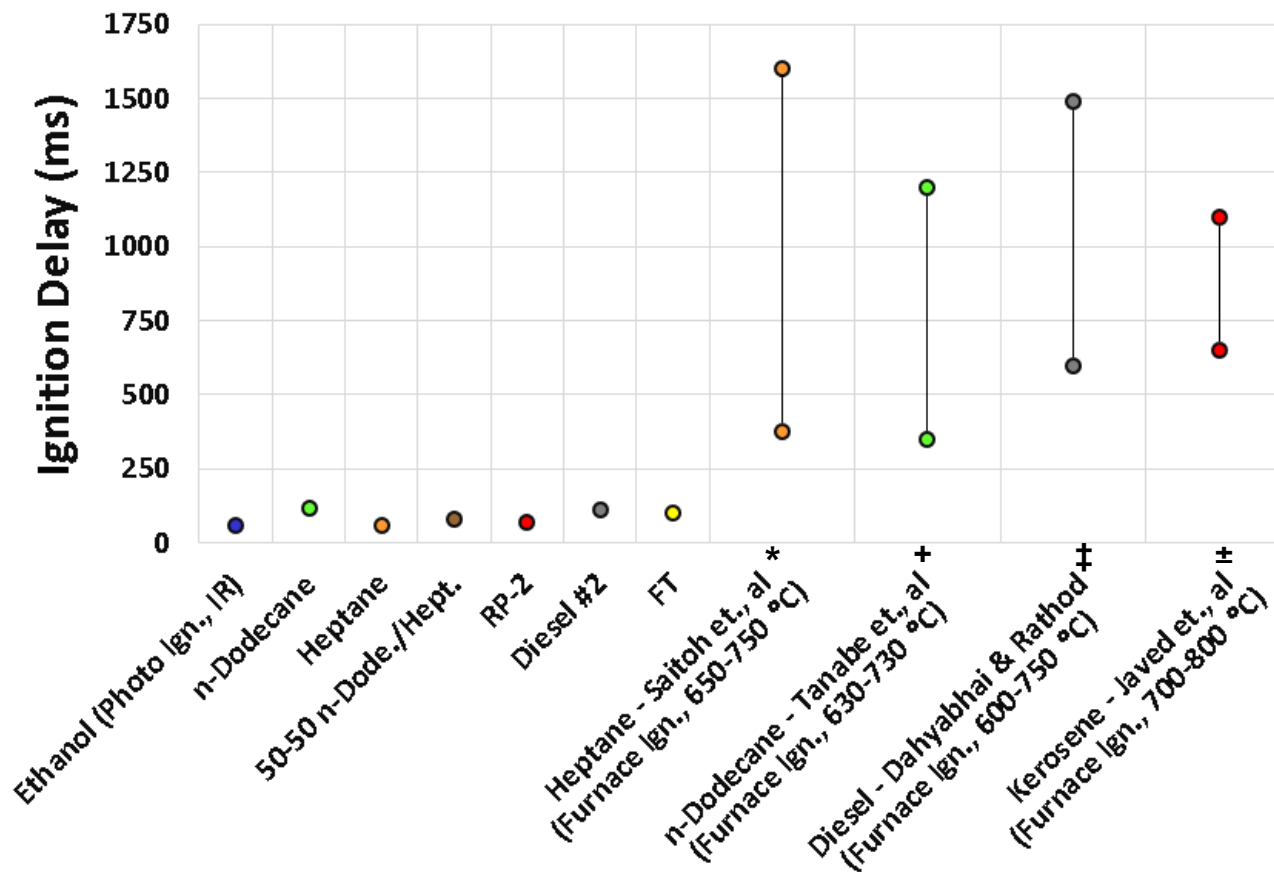


- Performed multiple series of 4-6 tests for each fuel to “estimate”  $\tau_{ign.}$  through visual inspection of high-speed images (no error bars.)
- Ignition delay was defined as the time from the Xe-flash to the initial flame appearing.



# Ignition Delay for Neat Fuel Droplets

(range of data from the literature is included)



\* Saitoh et., al, *Combustion and Flame* (1982)

+ Tanabe et., al, *Proc. Combust. Inst.* (1996)

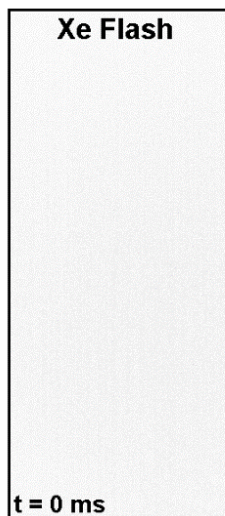
‡ Dahyabhai & Rathod, *IJAERD.* (2014)

± Javed et., al, *Intrn. Heat Transfer Symp.* (2014)

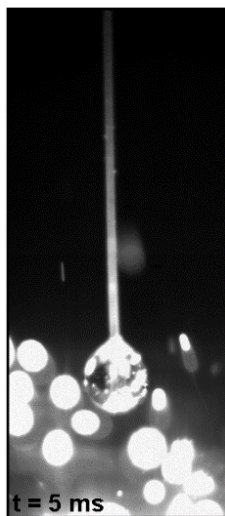
- Photoignition and plasma arc ignition provide a short duration ignition transient that typically lasts <120 ms for all fuels.
- Longer ignition delays are associated with slower ignition methods such as a heated wire or introducing droplet to hot surroundings/box.



# High-Speed Images of Droplet Ignition: Heptane as an Example



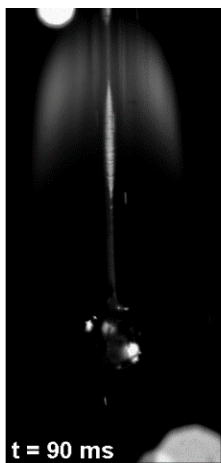
(a)



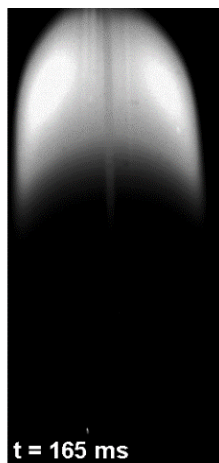
(b)



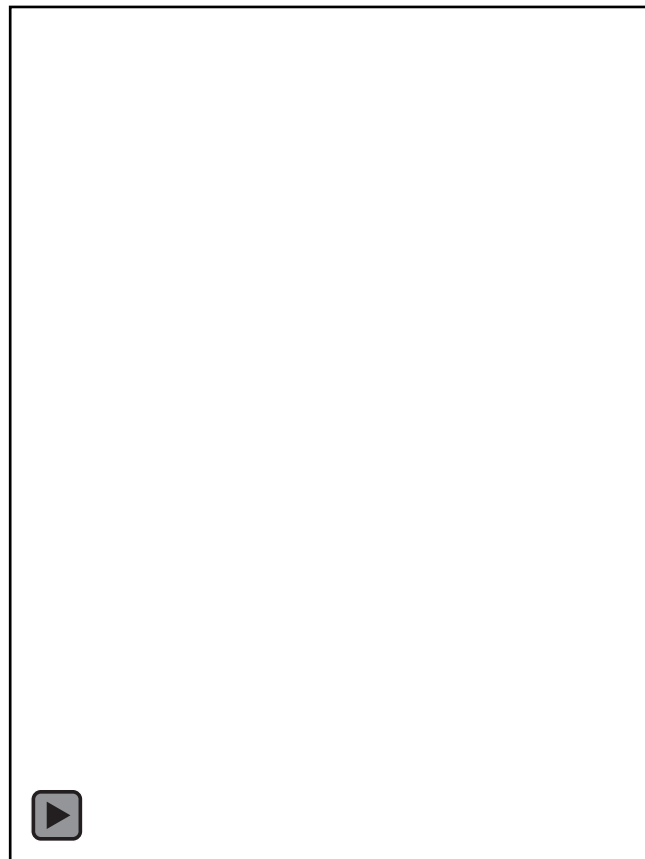
(c)



(d)



(e)





# Different Ways of Introducing Nanoparticles (NPs) as Fuel Additives



- Typical NP additives include metals, metallic alloys, their compounds/oxides and carbon nanostructures:
  - These additives may form a solid dispersant in hydrocarbon fuels, often requiring addition of an organic surfactant
  - Most of the work reported in the literature is focused on the above
  - Achieving nano-dispersion of NPs in most fuels is quite challenging
- Some energetic compounds such as ammonia-borane may partially dissolve in a fuel:
  - We have studied the above, but there are very few reports on such additives
- It is possible to dissolved an additive in a solvent and form a fine liquid emulsion with a hydrocarbon (HF) fuel:
  - We did not study the above and no reports on the this is found in the literature



# Study of $K$ for HC Nanofuels (mostly RP-2 & Ethanol + NP additives)

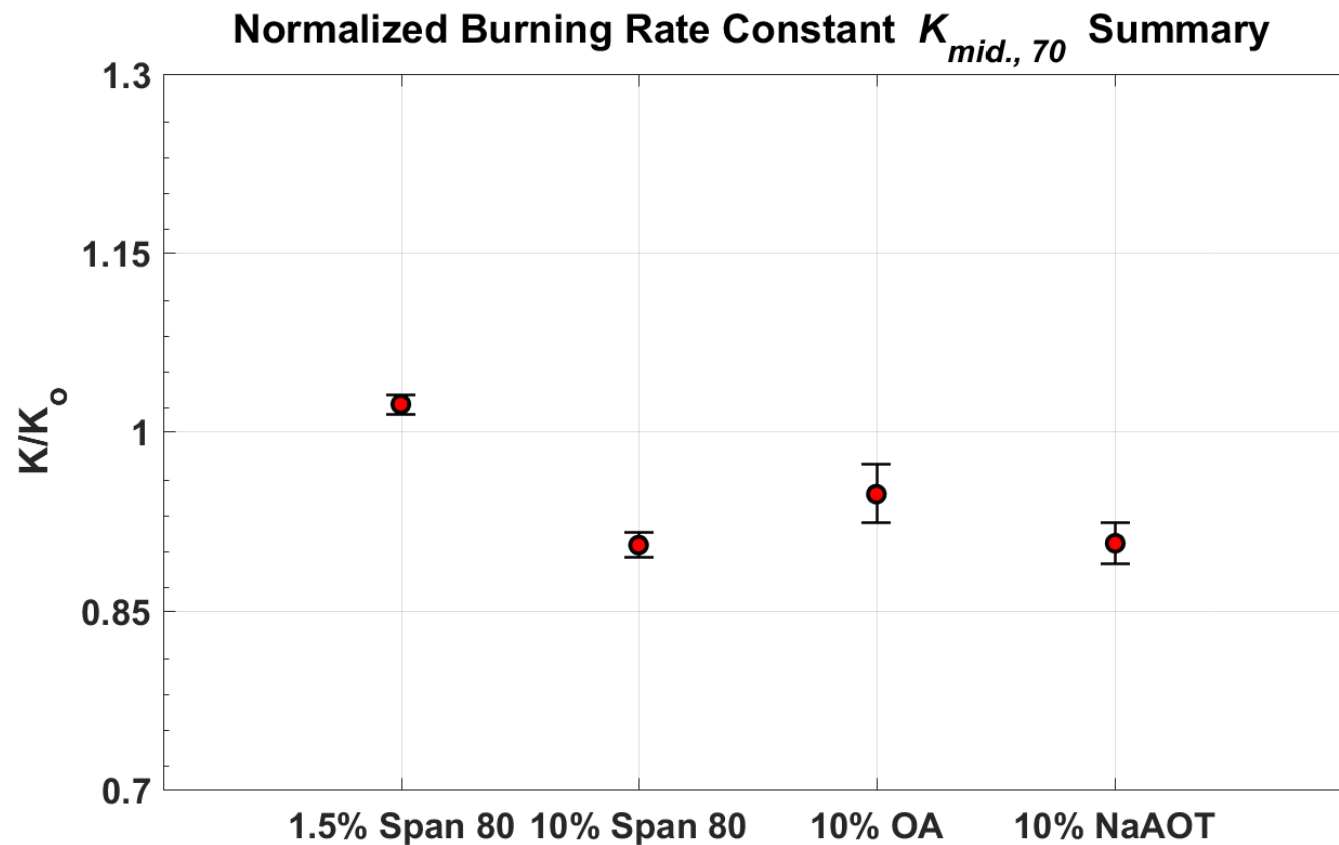


Guided by some recent reports, where they show sizable change in  $K$ , we performed series of 5-15 identical tests on suspended nanofuel (NF) droplets utilizing following NP additives:

- MgO: Based on the work of Bello et. al., (2015) RP-2 with MgO
- Graphene nano-platelet (GNP) additives: Based on the work of Ghamari et. al., (2017), Jet-A with graphene nano-platelets (GNP)
- B/Na-based soluble additives: Based on the work at Purdue, Pfeil et., al., (2013), Ethanol with Ammonia Borane
- nAl (80 nm): Based on the work performed at UCLA and others, different hydrocarbon fuels with nAl
- Graphene: Based on a sample from previous SBIR study for AFRL, RP-2 with graphene flacks additive



# Surfactant Addition Sensitivity: RP-2 (for most frequently used organic compounds)

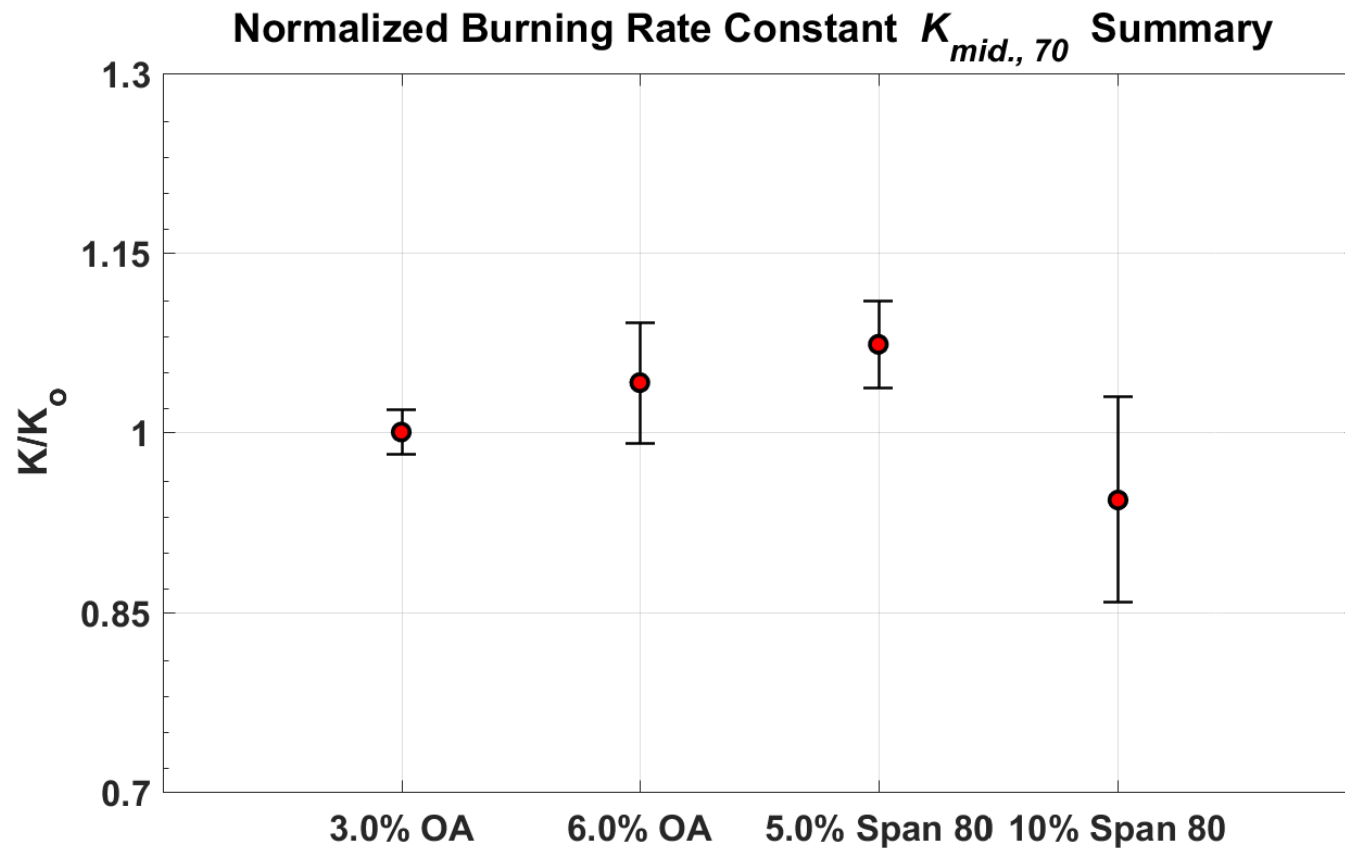


## RP-2-Surfactant Combinations

$K_{mid., 70}$  for RP-2 fuel with Span 80, Oleic Acid (OA) or Sodium Bis(2-Ethylhexyl) Sulfosuccinate (NaAOT) surfactant



# Surfactant Addition Sensitivity: Heptane



## Heptane-Surfactant Combinations

$K_{mid., 70}$  for Heptane ( $C_7H_{16}$ ) fuel with Oleic Acid (OA) or Span 80 surfactant (larger error bars are due to fewer tests in each case)





# Reported Work on RP-2/MgO\*



- They used 20 nm MgO dispersed in RP-2 using 1:10 wt ratio of Oleic Acid

Table 3. Time Durations (in Milliseconds) and Burn Rate Constants for Stages of Regression with Varying MgO Concentrations

- Ignition method was stationary Ni-Cr heating coil

- Initial droplet size: ~2 mm

- Fiber diameter: 1 mm

- Reported 270 fold increase for 0.5% MgO in RP-2\*

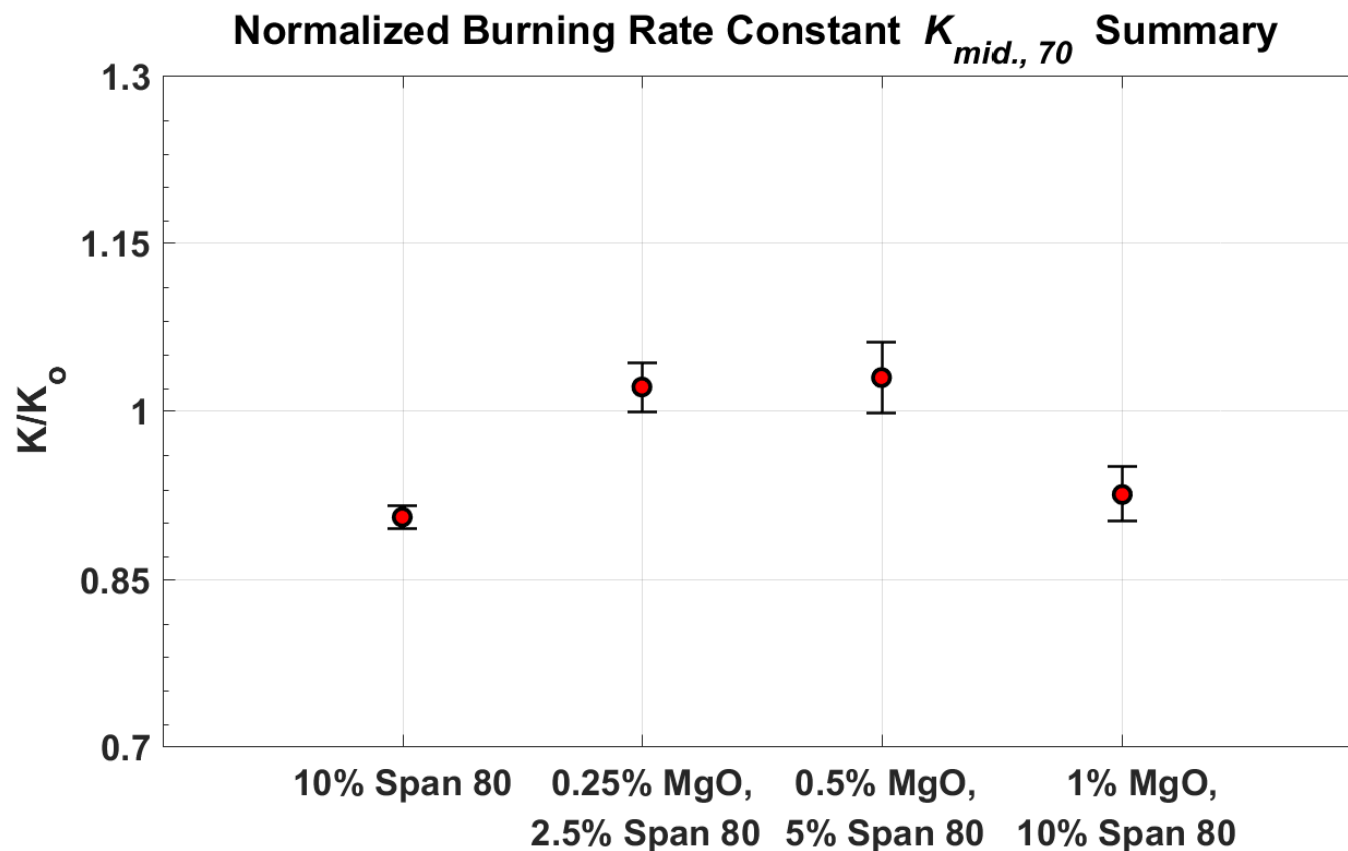
MgO (wt %)	stage 1 duration (ms)	stage 2 duration (ms)	$K_b$ stage 2 ( $\text{mm}^2/\text{s}$ )	stage 3 duration (ms)	$K_b$ stage 3 ( $\text{mm}^2/\text{s}$ )
0	300	830	0.414	N/A	N/A
0.05	92	98	8.554	170	0.46
0.25	19	11	69.97	19	2.85
0.50	3	3	111.8	4	47.59
0.75	9	8	16.95	12	53.67
1	122	328	3.075	719	2.71

Quasi-steady  
Burn Phase

\* All data from: Bello et. al, *Energy & Fuels* 29 (9), pp. 6111–6117, (2015)



# Evaluation of $K$ for RP-2/MgO



## RP-2 Nanofuel Combinations

$K_{mid., 70}$  for RP-2 fuel with Span 80 surfactant (10:1 wt Ratio) with varying MgO concentrations



# Reported Work on Jet-A and Graphene Nano-platelets (GNP)\*



- Used GNP dispersed in Jet-A kerosene, using 1.5% wt Span 80
- GNP Specification: 6-8 nm thick platelets with  $D \sim 5 \mu\text{m}$
- Ni-Cr heating coil ignitor
- Initial droplet size:  $\sim 2 \text{ mm}$
- Fiber size:  $3 \times 16 \mu\text{m}$  SiC fibers
- Reported  $\sim 7\%$  max increase at 0.1% wt. GNP that was attributed to absorption of heat by the darkened fuel

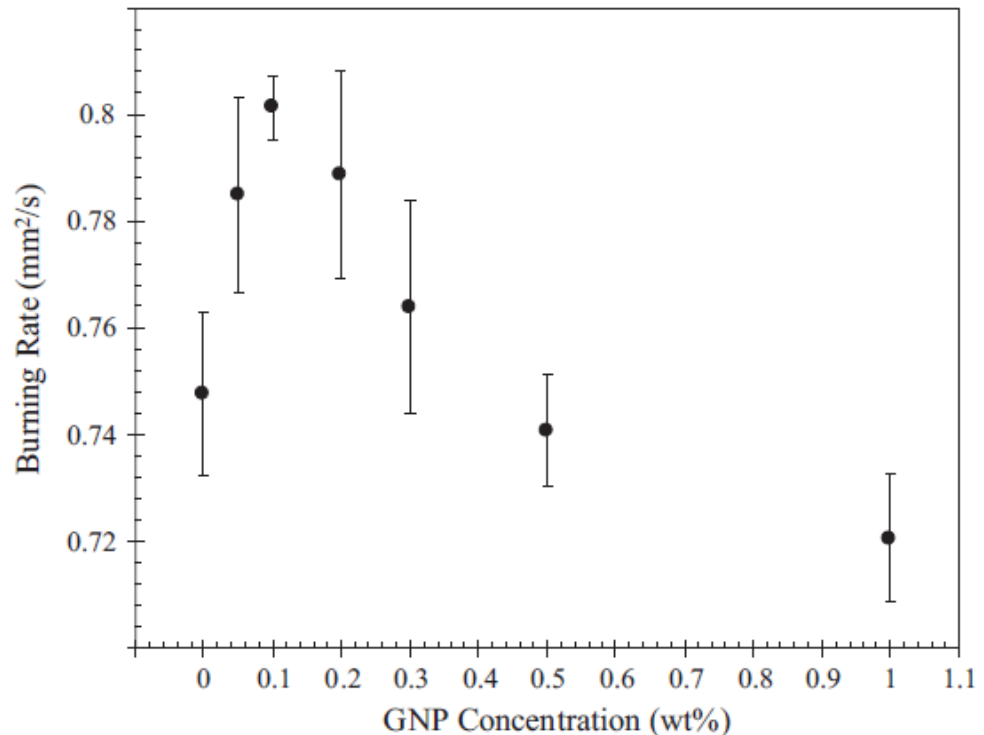
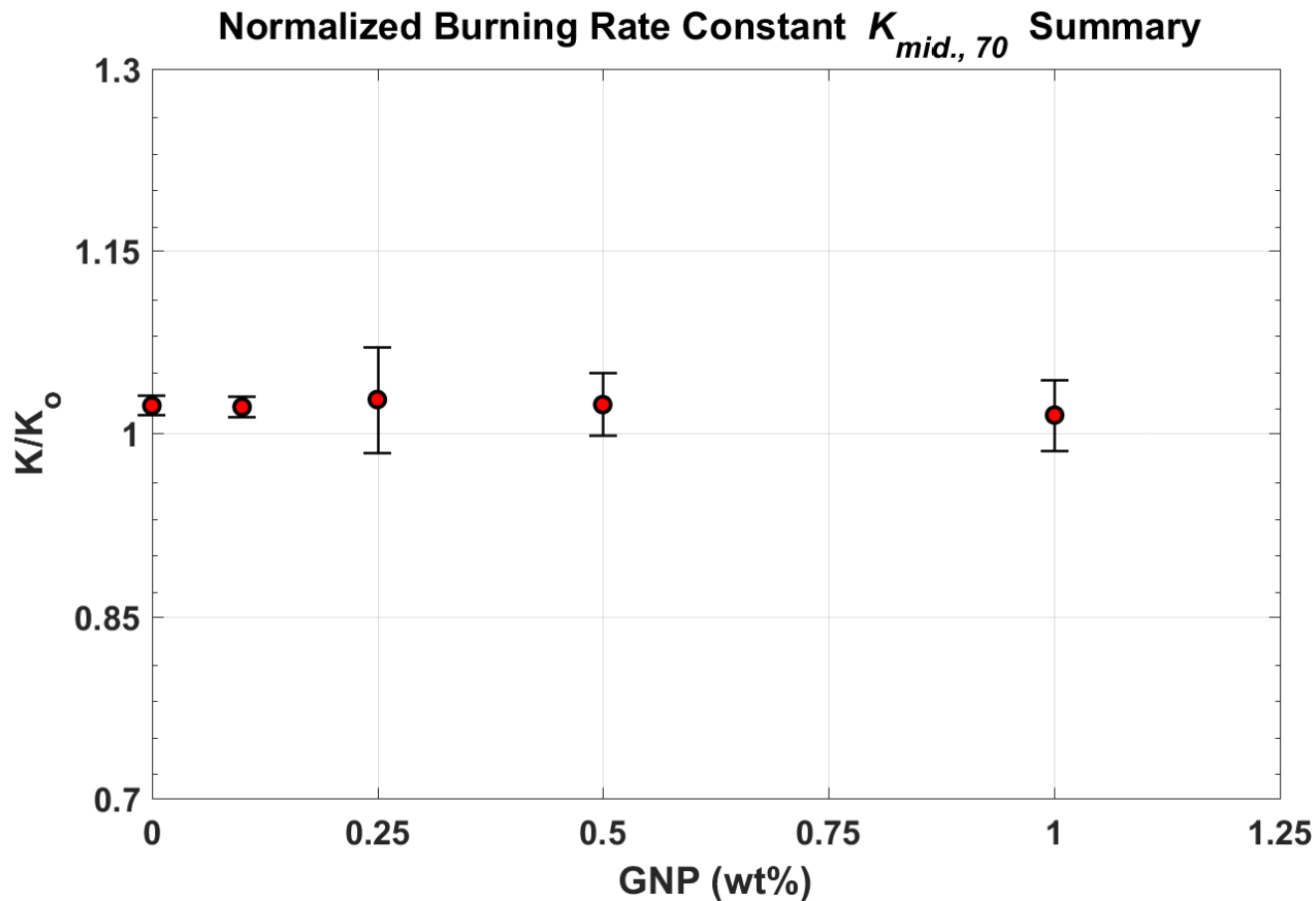


Fig. 9. Burning rate as a function of GNP concentration within jet fuel droplets. Each data point represents an average of at least five repetitions and the error bars show the corresponding standard deviation.

\* All data from: Ghameri et. al, *Fuel* 118, pp. 182–189, (2017)



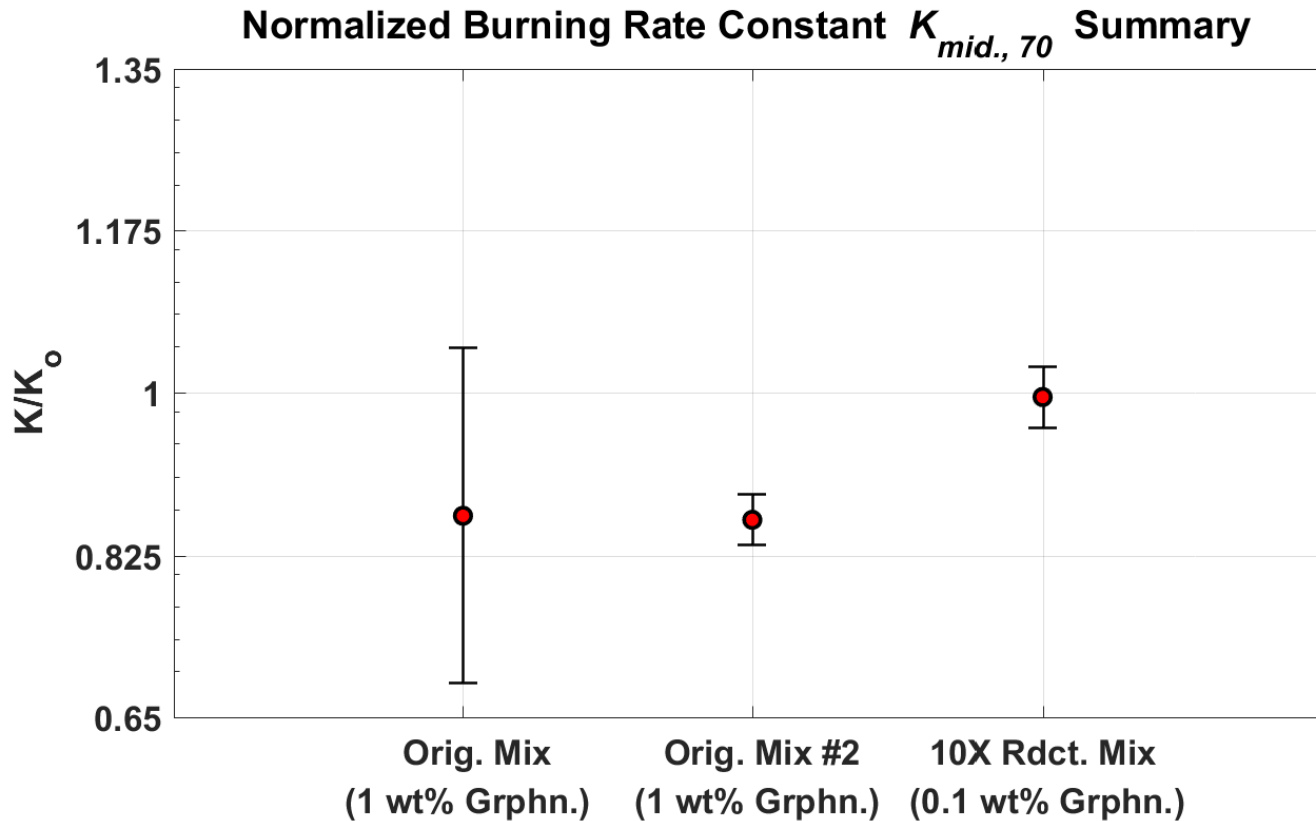
# Evaluation of $K$ for RP-2/GNP



$K_{mid., 70}$  for RP-2 and Span 80 (1.5% wt.) with low concentrations of GNPs  
Our fast-acting ignition and the exclusion of the first 15% of the burning curve minimizes any possible effects of the ignition method



# Evaluation of $K$ for RP-2/Graphene

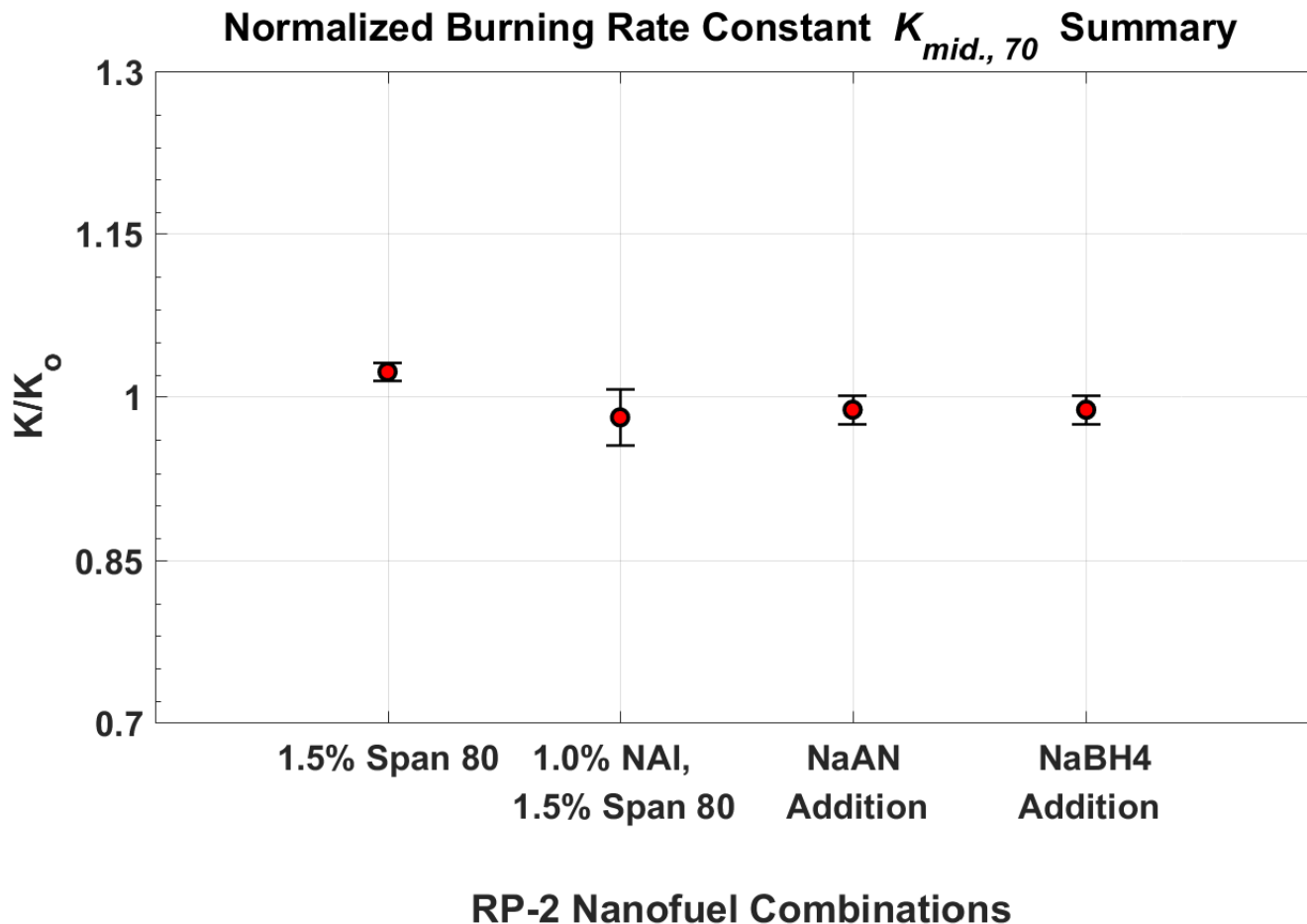


## RP-2-Graphene Nanofuel Combinations

$K_{mid., 70}$  for RP-2 and a surfactant with two different concentration of graphene  
The larger error bar is due to an uncertainty in the concentration of the original mix



# Evaluation of $K$ for RP-2 with Nano-Al (nAl) and Soluble Energetic Compounds

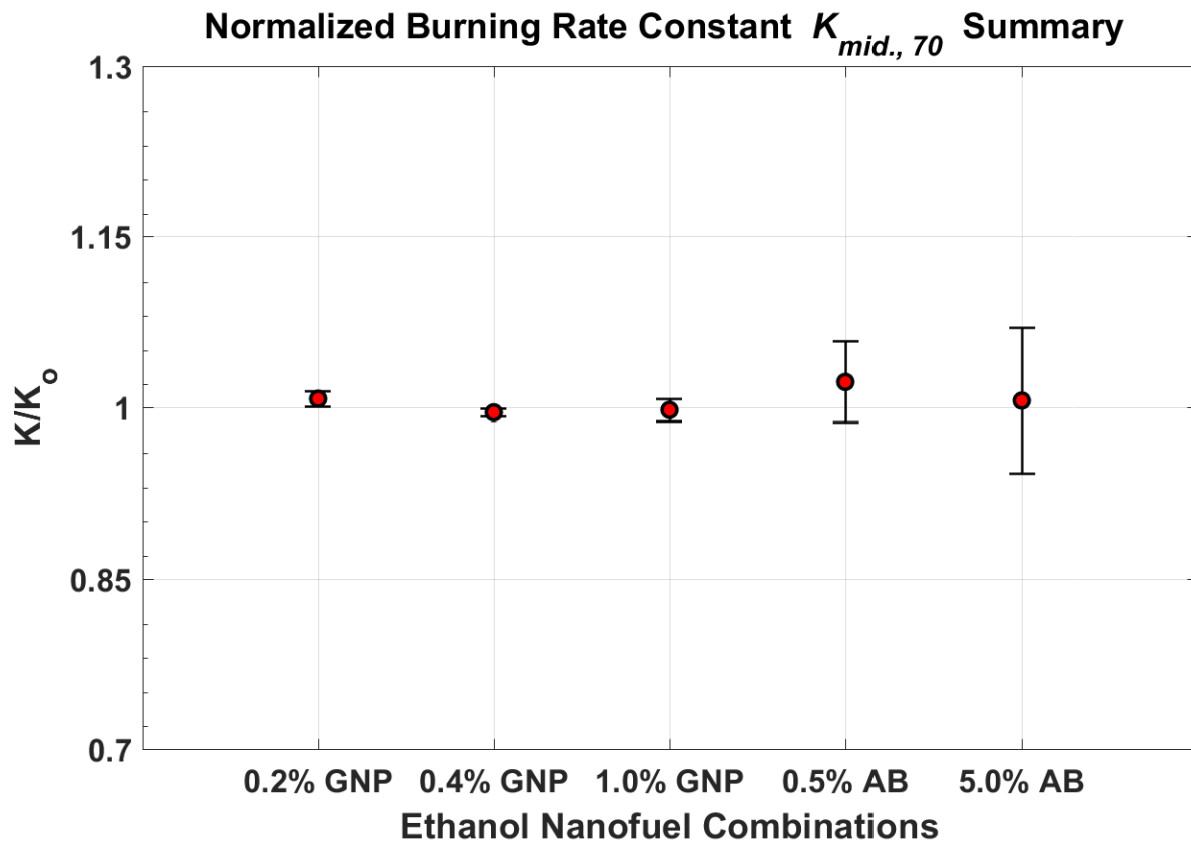


$K_{mid., 70}$  for RP-2 and Span 80 (1.5% wt.) with 80 nm nAl

The unknown concentration of NaAN and NaBH4 was the Max. that was soluble in RP-2



# Evaluation of $K$ for Various Ethanol Nanofuels

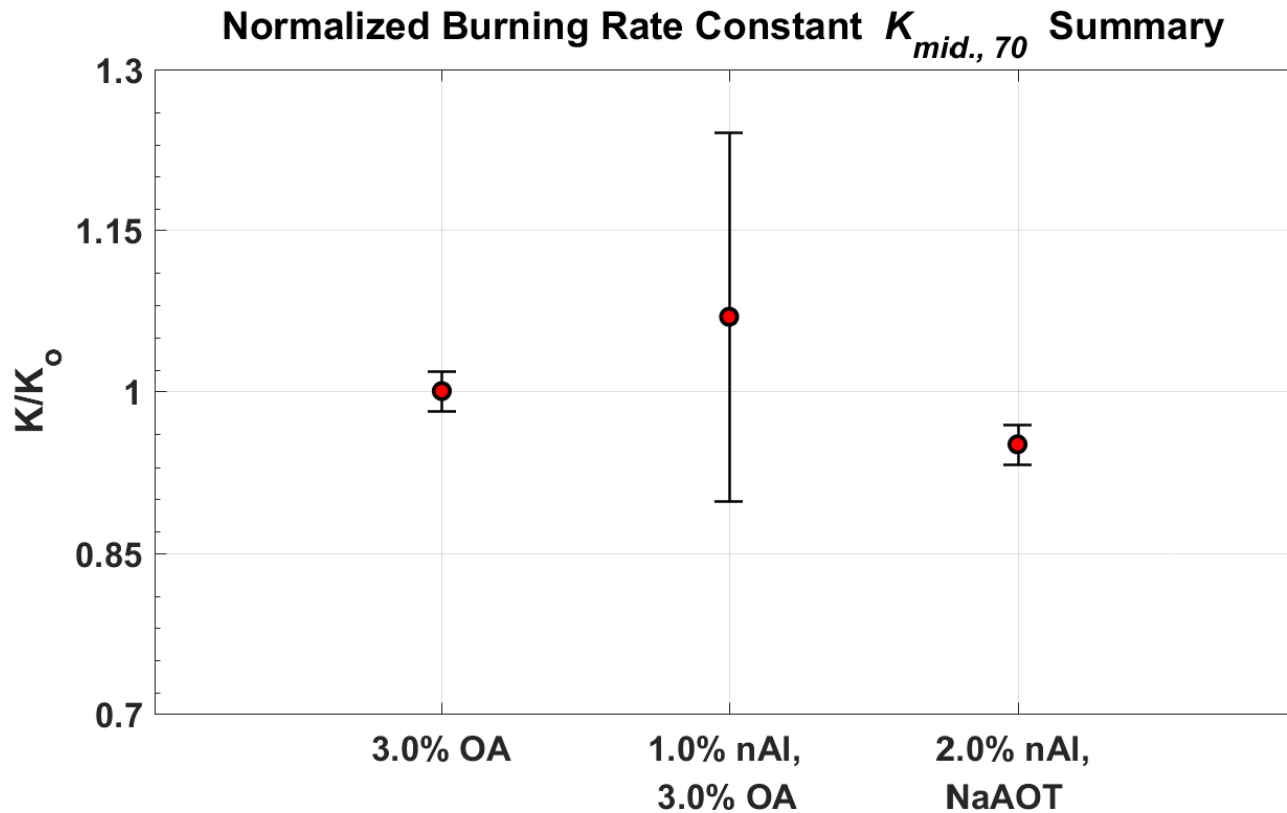


- $K_{mid., 70}$  for ethanol with varying GNP and Ammonia Borane concentrations (no surfactant)
- Pfeil, et. al., *Combustion and Flame* (2013), reported 16% increase in  $K$  for 6% AB (the Max. solubility of AB in Ethanol)





# Evaluation of $K$ for Heptane with nAl



## Heptane Nanofuel Combinations

$K_{mid., 70}$  for heptane fuel with oleic acid (OA) or NaAOT as a surfactant  
oleic acid produced relatively poor suspension of nAl in heptane



# Conclusions



## **Burning Characteristics of Suspended Droplets of Neat Fuels:**

- New fast-acting ignition methods provide well defined measures of burning rate constants,  $K$ , and ignition delays in hydrocarbon fuel droplets.
- Burning rate constants,  $K$ , measured well after ignition transient and they are unaffected by the ignition method.
- $K$  for neat fuels are in general agreement with the values reported by others
- Measured ignition delays are much shorter than reported values in the literature obtained by more conventional methods (where substantial heating is involved.)

## **Burning Characteristics of Suspended Droplets of Nanofuels:**

- Effect of addition of modest amount of surfactants on  $K$  is minimal
- For moderately loaded nanofuels (<5%) the change in burning rate constant is relatively small (<10%).
- Effects of most additives are only noticed later in droplet lifetime when the NPs become concentrated
- We observed little change in  $K$  for dissolved NFs, but have seen qualitative effects such as change in flame color and foaming of the fuel at the end.



# Backup Slides

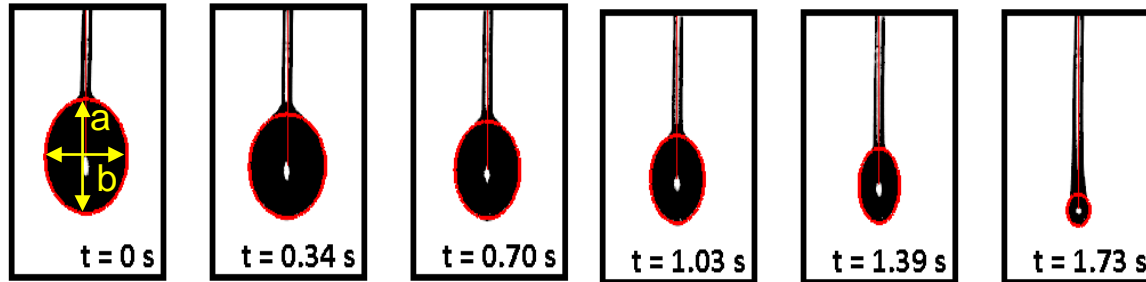




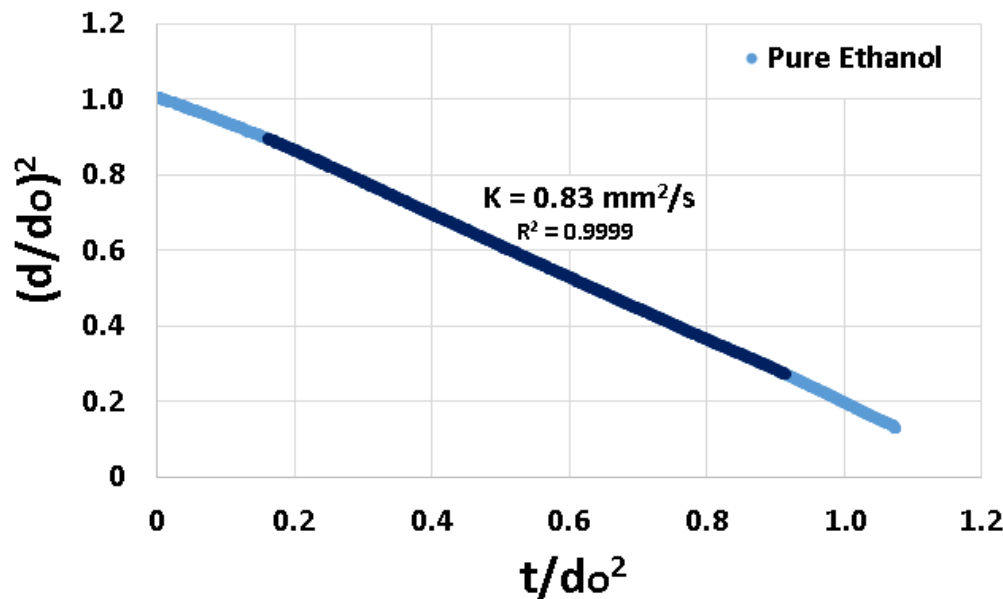
# Droplet Regression and Evaluation of $K$ (Ethanol Example)



## Droplet Burning Time Sequence



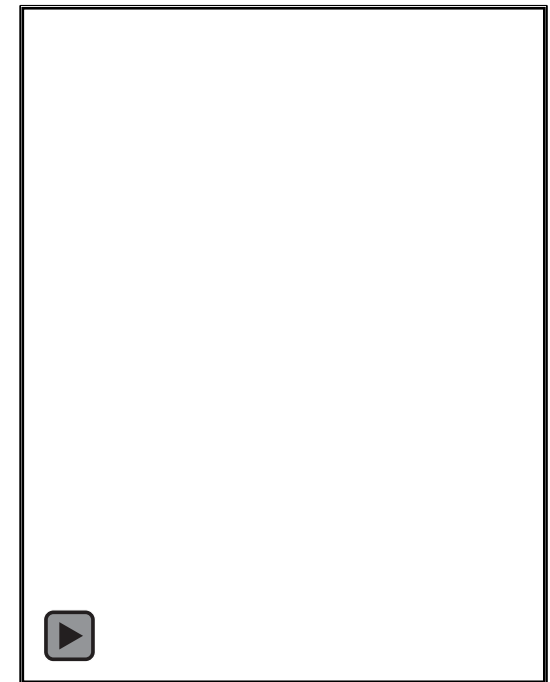
## Normalized Droplet Regression



## Burning Rate $K$ Calculation

$$K = \frac{d}{dt} (d_{eqvs})^2, \text{ where}$$

$$d_{eqvs} = 2a^{2/3}b^{1/3}$$



Ethanol Droplet Burning.



# Ignition Delay in Fuel Droplets



- Ignition delay ( $\tau_{ign.}$ ) is typically defined as the time a droplet is introduced to a hot environment until the droplet flame becomes fully established\*.
  - Traditionally thought of a property of the fuel.
  - $\tau_{ign.}$  decreases as  $T_{l.s.}$  increases (data available up to 1300 K.)
  - $\tau_{ign.}$  decreases as  $P_c$  increases (planned for future works.)
- All of the above trends were observed via introducing the droplet to a hot environment/filament relatively slowly,  $>0.5$  s.
- Under such conditions, a direct/visual indication of the onset of combustion is impractical due to luminous background.
- However, reasonable estimates of  $\tau_{ign.}$  for fuel droplets can be achieved using photoignition and plasma arc ignition.

\* Aggarwal, *Progress in Energy and Combustion Science* (2014)